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MANUFACTURE OF CELLULOSIC PRODUCTS

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Granted to Kimberly-Clark Corporation, Neenah, Wisconsin,
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from binder
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No. OF CLAIMS 4

This invention relates to the recovery of paper-making fibers and pigments from coated paper and more particularly to a process for such recovery.

5 A major object of the invention is to provide an improved process for reclaiming fibers and pigments from paper which has been coated with a substantially water-proof protein-bonded coating.

10 A further object is to provide a process for reclaiming protein-bonded coated paper under conditions which promote rapid disintegration of the coating, the process being carried out more effectively and with less degradation of desirable properties in the recovered pulp than has been possible heretofore.

15 These and other objects will become apparent from the following description and accompanying drawings.

In the drawings:

Fig. 1 is a graph showing the effect of varying the enzyme concentration in the recovery process.

20 Fig. 2 is a graph showing the effect of hydrogen ion concentration on the time required for the recovery process.

Fig. 3 is a similar graph illustrating the time-temperature relationship for the process.

25 In the manufacture of paper, it is desirable to reuse, with a minimum of loss, the waste paper or "broke" which results during the normal course of production. The disintegration of paper broke to a fibrous state is

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usually accomplished by chemical or mechanical means, or
a combination of both, the resultant pulp suspension
being returned to the papermaking cycle without further
processing. Repulping conditions are preferably of such
5 a nature that the cellulose fibers in the broke will be
separated from one another and from the various non-
fibrous constituents of the paper, with a minimum amount
of mechanical or chemical damage to the fibers. Usually,
the repulping of broke obtained in normal papermaking
10 processes does not impose a serious problem. However,
a repulping problem does arise in the production of
certain coated papers used for high quality offset
printing wherein the paper is coated with a substantially
water-resistant coating in which the adhesive or binder
15 for the coating pigment consists of a hardened protein.
Methods for repulping this substantially waterproof
coating, using normal techniques have not been entirely
satisfactory.

Broke which contained hardened protein binder in
20 the coating has commonly been repulped by using relatively
strong caustic solutions at substantially high tempera-
tures. Such severe treatment was believed necessary
mainly to break up the coating flakes which form as the
broke is being slushed. Since the cellulose fibers in the
25 paper being reprocessed were subjected to the usual
pulping, bleaching, and refining operations, considerable
surface area of the fibers is exposed to the penetration

and action of chemicals during repulping, hence, the severe conditions imposed by the strong caustic and high temperature results in some cellulosic breakdown and considerable loss of fiber.

5 The action of alkalis during paper reprocessing has additional undesirable effects when groundwood pulp fibers are among the fibers present in the paper being treated. The groundwood fibers have large quantities of lignin present causing the reprocessed pulp to be
10 darkened by the action of the alkali with a substantial loss in overall brightness. These fibers then must undergo an additional costly bleaching step, or have high cost filler pigments added, in order to bring the pulp up to a suitable brightness level before reintroducing the
15 recovered fibers into the papermaking furnish.

 The invention taught herein insures rapid and effective disintegration of paper broke having a protein-bonded coating, with substantially no degradation of the desirable properties in the recovered pulp.

20 Coated papers used for offset printing, require a finish or top coating which is substantially water resistant. Such coatings are usually applied as an aqueous suspension of a mineral pigment and a proteinaceous adhesive binder having water-resistant properties
25 when dried. Binders usually employed as the adhesive in these paper coatings are casein and soya bean protein. Such protein-bonded coatings are insolubilized by reacting

the protein with formaldehyde or a formaldehyde donor material added either before or after the coating is applied to the paper. The insolubilizing reaction is promoted by heat applied during the drying stage, and
5 continues for some period thereafter as a result of natural aging.

The reprocessing of coated printing papers, the coating of which includes a hardened protein binder, has heretofore fallen short of complete success due to difficulties encountered in respect to the dissolution of the proteinaceous content of the coating. Solutions heretofore proposed have either been found impractical for
10 employment in existing equipment or have presented undesirable side effects. The industry has long sought an effective solution to this problem in order to permit the process to be conducted in existing plants without requiring modification of process equipment and without imposing impractical operating conditions. This invention
15 teaches employment of proteolytic enzymes for the effective hydrolyzation and dissolution of the above-mentioned hardened protein binder and the subsequent recovery of essentially all the fibers and pigments originally present in the paper being reprocessed. The inventive process
20 can most effectively be practiced under the closely controlled conditions of hydrogen ion concentration, temperature and enzyme concentration below taught.
25

Enzymes suitable for use in the present process are of the proteolytic type. Of these, the plant enzyme proteases such as papain, ficin, bromelin, malt enzymes, and the like are generally preferable although animal enzyme proteases such as pepsin, trypsin and homotrypsin may be used.

As shown in Fig. 1, repulping of the coating within a reasonably short time, requires an enzyme concentration of at least 0.5% by weight on the dry weight of the broke. Where time is less important, the enzyme concentration may be as little as 0.25%. As the enzyme concentration in the stock suspension is increased the time necessary to hydrolyze the coating decreases. For economic reasons, a practical top limit of enzyme concentration of 2.0% in the pulp suspension, based on the weight of the broke, is preferred. However, higher concentrations can be used when the situation demands it.

In carrying out the process, the waste paper or broke having a protein-bonded coating is charged into a beater or repulper such as is used in convention paper-making processes. Water having a temperature sufficient to maintain the mixture at between 40° C. and 60° C. is added to the broke charge in sufficient quantity to partially disintegrate the broke and obtain a suspension of pulp of between about 2% and 10% consistency. To this stock suspension there may be added a minor percentage of sodium sulfite, and a minor percentage of a sequestering and dispersing agent, including various sodium salts of phosphate and silicate. When necessary, the pH of the suspension is adjusted to between 6 and 8 by the addition of an acid such as HCl, or an alkali, such as caustic soda. The proteolytic enzyme is added after all other preparatory adjustments have been made so that its full effectiveness may be utilized. The resulting mixture is maintained at a temperature of between 40° and 60° C. and agitated until the coating flakes are substantially disintegrated by hydrolysis and dissolution of the protein. Under the above conditions, the time required for complete disintegration of the coating flakes is approximately one hour or less. The pulp thus obtained is suitable for reuse in the papermaking process without further treatment. The enzyme present in the repulped material is killed by the alum normally present in the fresh furnish, by the formaldehyde in the subsequently applied coating, or by the high temperatures to which the coated sheet is subjected on the paper machine dryers.

Fig. 2 shows that the optimum pH for repulping is 7.0. However, the pH may be varied from about 6.5 to 8.0 without appreciably increasing the disintegration time.

5 Fig. 3, shows the optimum temperature for repulping to be 50°C. The temperature may be varied from about 40°C. to about 60°C. without appreciably affecting the optimum disintegration time.

Although the use of a proteolytic enzyme only in the repulping solution works satisfactorily, it has been
10 found that certain additives increase the rate of reaction. For example, a minor percentage of sodium sulfite accelerates the enzymatic action. The percentage of sodium sulfite which is effective may vary from between about 0.25% to 1.0% by weight based on the dry weight of the
15 broke. The beneficial effect of the sodium sulfite is believed to result from its action in removing residual chlorine from the water, in breaking formaldehyde cross-linkages with the protein, and in tying up the formaldehyde so that it cannot inhibit the action of the enzyme.

20 Sequestering and dispersing agents, such as various sodium phosphate and silicate salts, also increase the effectiveness of the enzymatic action in the repulping process. For example, sodium hexametaphosphate, sodium pyrophosphate, trisodium phosphate, and sodium silicate are
25 effective in quantities from about 0.25% to 2% on the dry weight of the fiber.

The following examples are set forth for purpose of illustration rather than limitation of the concept.

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EXAMPLE I

Paper having an initial basis weight of 53 pounds per 25" x 38" 500 sheet ream and having a furnish of about 20% bleached sulfite and about 80% bleached kraft fibers, was coated on both sides with an aqueous coating containing about 48% solids consisting of about 90 parts by weight of coating clay, 10 parts of TiO_2 , 25 parts of starch binder, and 3 parts melamine formaldehyde resin. This coating was applied at the rate of about 7.5 pounds per side per ream. After the first coating was dried, a second coating was applied on both sides of the paper. The second coating consisted of an aqueous dispersion containing about 57% solids consisting of approximately 88 parts by weight of coating clay, 12 parts TiO_2 , 18 parts of soya bean protein binder, 6 parts latex and 6 parts hexamethylene tetramine (the latter based on the weight of the protein). The second coating was applied at the rate of about 6 pounds per side per ream. The paper was subsequently dried by passing it over a series of heated cylinders. 4000 pounds of paper broke, coated as described above, was loaded into a conventional repulper. Warm water and steam sufficient to maintain the temperature at 50° C. were added in sufficient quantity to obtain a suspension of pulp of about 5% consistency. 0.5% by weight of sodium sulfite, and 0.5% by weight of sodium hexametaphosphate were added to the pulp suspension. A small amount of caustic soda solution was added to the suspension

to bring the initial pH to 7.0. 0.5% of a proteolytic enzyme (Serizyme) by dry weight of the broke, based on the liquid weight of the enzyme as purchased, was then added to the suspension. Serizyme is the trade name for a proteolytic enzyme preparation manufactured by the Wallerstein Co. Periodic samples were taken to determine when disintegration was complete. After a period of about three quarters of an hour of agitation, the paper and coating were completely disintegrated and returned to the papermaking furnish without further treatment.

EXAMPLE II

Paper having an initial basis weight of 37 pounds per 25" x 38" 500 sheet ream and having a furnish about 60% bleached sulfite fibers, 20% bleached kraft fibers and 20% bleached groundwood fibers was coated on one side with an aqueous coating containing about 40% solids consisting of about 86 parts by weight of coating clay, 6 parts bentonite, 8 parts TiO_2 , and 30 parts of starch binder. The coating was applied at the rate of about 7 pounds per ream. The first coating was dried and a second coating applied over the first consisting of an aqueous dispersion containing about 57% solids consisting of approximately 92 parts by weight of clay, 8 parts TiO_2 , 16 parts soya bean protein binder, 6 parts latex, and 6 parts hexamethylene tetramine (the latter based on the weight of the protein). The second coating was applied at the rate of 11 pounds per ream. The coated paper was subsequently dried as in Example I.

4000 pounds of the paper broke, coated as described above, was loaded into a conventional repulper. Warm water and steam sufficient to maintain the temperature at about 50° C. were added in sufficient quantity to obtain a suspension of pulp of about 5% consistency. 0.5% by weight of sodium sulfite, and 0.5% by weight of sodium hexametaphosphate were added to the pulp suspension. A small amount of caustic soda solution was added to the suspension to bring the initial pH to 7.0. 0.5% of a proteolytic enzyme (Serizyme) by dry weight of the broke, based on the liquid weight of the enzyme as purchased, was then added to the suspension. The temperature of the pulp suspension was maintained at 50° C. Periodic samples were taken and after a period of about one half hour of agitation, the paper and coating were found to be completely disintegrated. There was no loss in brightness in the pulp, even though groundwood fibers were present, and the resulting pulp was returned to the papermaking furnish without requiring additional treatment.

EXAMPLE III

Paper having an initial basis weight of 53 pounds per 25" x 38" 500 sheet ream and composed of about 20% bleached sulfite and about 80% bleached kraft fibers, was coated on both sides with an aqueous coating having a solids content of about 40% consisting of about 90 parts by weight of coating clay, 10 parts of TiO_2 , 25 parts of starch binder, and 3 parts melamine formaldehyde resin.

The coating was applied at the rate of about 7.5 pounds per side per ream. After the coating was dried, a second coating was applied to both sides of the paper. The second coating consisted of an aqueous dispersion of about 57% solids consisting of approximately 88 parts by weight of coating clay, 12 parts TiO_2 , 18 parts of casein binder, 6 parts latex and 6 parts hexamethylene tetramine (the latter based on the weight of the protein). The second coating was applied at the rate of about 6 pounds per side per ream. The coated paper was subsequently dried as in Example I.

4000 pounds of paper broke, coated as described above, was loaded into a conventional repulper. Warm water and steam sufficient to bring the temperature to about 50°C . were added in sufficient quantity to obtain a suspension of pulp of about 5% consistency. 0.5% by weight of sodium sulfite, and 0.5% by weight of sodium hexametaphosphate were added to the pulp suspension. A small amount of caustic soda solution was added to the suspension to bring the initial pH to 7.0. 0.33% of a proteolytic enzyme (Rhozyme PF) by dry weight of the broke, based on the dry weight of the enzyme as purchased, was then added to the pulping suspension. Rhozyme PF is the trade name for a proteolytic enzyme preparation manufactured by the Rohm & Haas Co. The temperature of the pulp suspension was maintained at 50°C . Periodic samples were taken, and after a period of about three quarters of an hour of agitation, the paper and coating

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were found to be completely disintegrated. The repulped material was then returned to the papermaking furnish without further treatment.

5 Other methods and means of applying the principles of this invention may be used without departing from its spirit or scope as specifically define in the appended claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for recovering papermaking fibers and pigments from paper broke coated with a mineral pigment bonded by a formaldehyde-insolubilized protein which comprises the steps of adding warm water to said broke in an amount sufficient to partially disintegrate said broke and obtain an aqueous suspension thereof having a consistency of from 2 to 10%, adding to said suspension, while maintaining the temperature thereof at between about 40°C. and 60°C. and the pH thereof at between 6 and 8, a proteolytic enzyme in an amount of at least 0.25% by weight based on the dry weight of said broke, agitating said suspension until the protein material is substantially hydrolyzed and dissolved, whereby the fibers and pigments in said paper broke are substantially completely separated and available for reuse in the paper-making process without further treatment.

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2. A process for repulping paper broke having a substantially waterproof protein-bonded coating in which the protein is insolubilized by formaldehyde which comprises hydrolyzing the protein binder in said coating by reducing said paper broke to a pulp suspension of about 2% to about 10% consistency in a heated aqueous solution having an initial pH of from about 6 to about 8 and containing at least 0.25% of a proteolytic enzyme, from about 0.25% to about 1.0% of sodium sulfite, and from about 0.25% to about 2.0% of a sodium phosphate, all based on the dry weight of the paper broke, maintaining the temperature of the pulp suspension between about 40°C. and about 60°C. and agitating said suspension for a period of from about one half to about one hour to substantially disintegrate the coating.

3. A process for repulping paper broke having a substantially waterproof protein-bonded coating in which the protein is insolubilized by formaldehyde which comprises hydrolyzing the protein binder in said coating by reducing said paper broke to a pulp suspension of about 2% to about 10% consistency in a heated aqueous solution having an initial pH of about 6 to about 8 and containing from about 0.25% to about 2.0% of a proteolytic enzyme, from about 0.25% to about 1.0% of sodium sulfite, and from about 0.25% to about 2.0% of a sodium salt selected from the group consisting of sodium hexametaphosphate, sodium pyrophosphate, trisodium phosphate and sodium silicate, all based on the dry weight of the paper broke, maintaining the temperature of the pulp suspension at between about 40°C. and 60°C., and agitating said suspension until the coating is substantially disintegrated.

4. A process for the recovery of papermaking fibers and pigments from coated paper broke, the coating of which includes a formaldehyde-insolubilized protein binder, which comprises hydrolyzing the protein binder by reducing said paper broke to a pulp suspension of about 5% consistency in a heated aqueous solution having an initial pH of 7 and containing about 0.5% of a proteolytic enzyme, about 0.5% of sodium sulfite, and about 0.5% of sodium hexametaphosphate, all based on the dry weight of the paper broke, maintaining the temperature of the pulp suspension at about 50°C., and agitating said suspension for a period of from about one half to about one hour to substantially disperse the coating.

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THIS CHART SHOWS THE EFFECT ON TIME
FOR COMPLETE DISINTEGRATION OF
PROTEIN-BONDED COATING BY VARYING THE
TEMPERATURE OF A REPULPING SOLUTION
HAVING THESE FIXED CONDITIONS: 0.5% Na_2SO_3
0.5% Na_3PO_4
0.5% ENZYME
5.0% CONSISTENCY
 $\text{pH}=7.0$

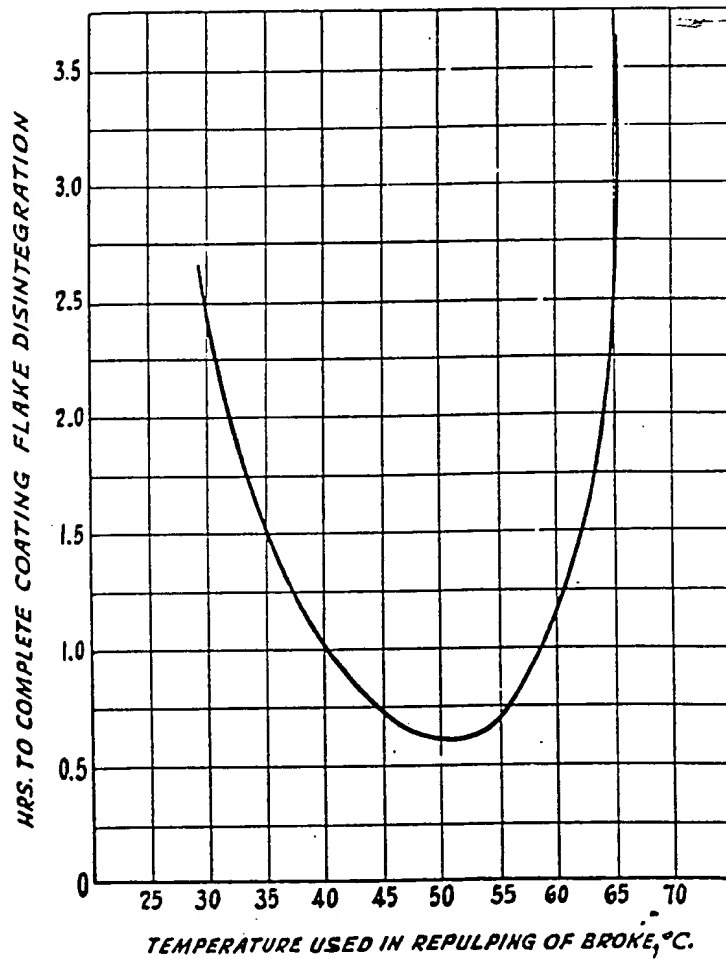


FIG.3.

THIS CHART SHOWS THE EFFECT ON TIME
FOR COMPLETE DISINTEGRATION OF
PROTEIN-BONDED COATING BY VARYING
THE pH OF A REPULPING SOLUTION
HAVING THESE FIXED CONDITIONS:

0.5% Na_2SO_3
0.5% Na_2PO_3
0.5% ENZYME
5.0% CONSISTENCY
TEMP. = 50° C.

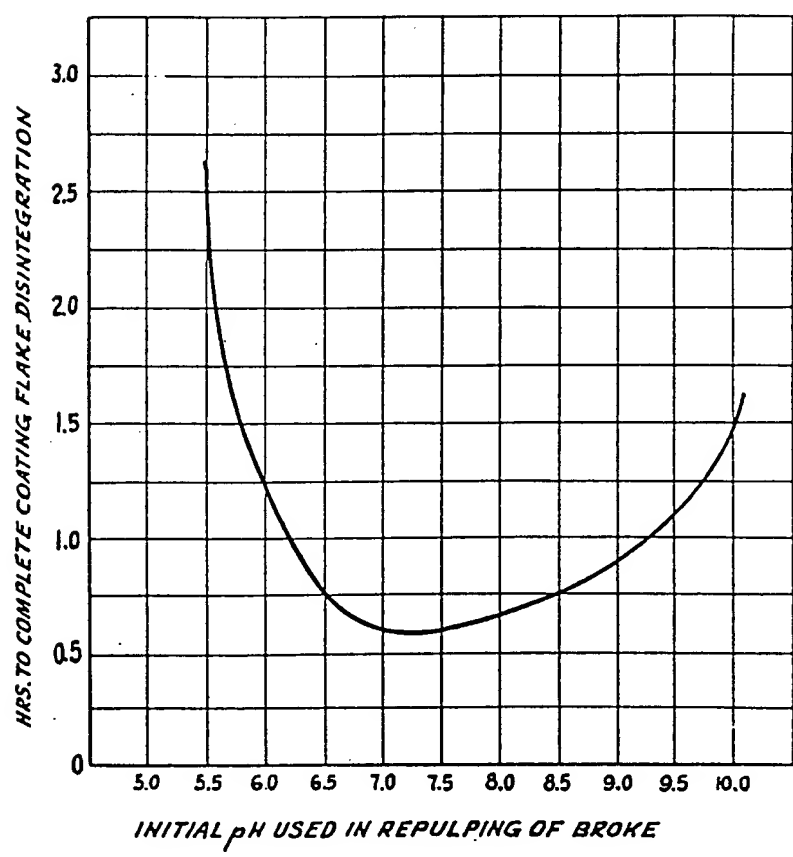


FIG.2.

THIS CHART SHOWS THE EFFECT ON TIME
FOR COMPLETE DISINTEGRATION OF
PROTEIN-BONDED COATING BY
VARYING THE PERCENT OF ENZYME
IN A REPULPING SOLUTION HAVING THESE
FIXED CONDITIONS: 0.5% Na_2SO_3
0.5% Na_2PO_3
5.0% CONSISTENCY
TEMP. = 50°C.
pH = 7.0

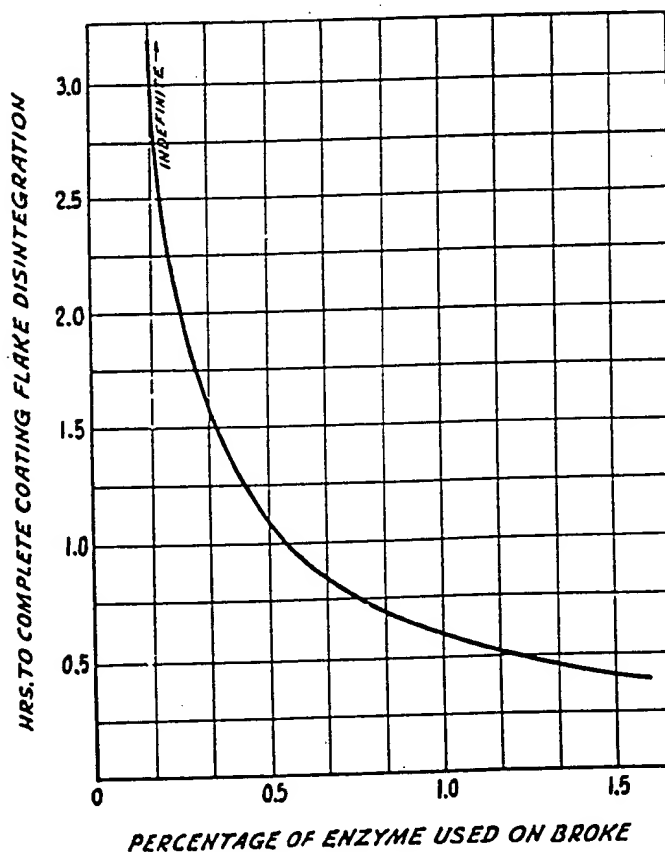


FIG.1.